

# **The Rheology of Cementitious Materials**

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# The Rheology of Cementitious Materials

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## Abstract

The introduction of a new generation of dispersants in concrete allow this material to exhibit self-compacting properties in its fresh state and high durability and mechanical strength in its hardened state. These properties translate into many practical advantages for the construction field. Two of the most important are reducing the ecological impact of this sector of industry and reducing the labor-intensive work associated with placing ordinary concrete by vibration. In this article, it will be shown that knowledge of colloidal science has proven essential in the development of this new generation of dispersants for concrete. Indeed, the polymer molecules used in these dispersants are specifically designed to induce steric repulsion between cement particles, reducing their agglomeration and allowing high workability of fresh concrete prior to setting. While the linkage between interparticle forces and the rheological behavior of cement pastes is still only semiquantitative, recent advances in the modeling of concrete rheology show very promising results in terms of handling aggregates with a wide distribution of particle sizes and shapes. However, accurate modeling requires reliable input on the interaction of the dispersant with the hydrating cement at the molecular level, which is identified as a future research challenge.

**Keywords:** cement, colloids, construction materials, rheology, aggregates.

## Introduction

When explaining what concrete is to students, the analogy to baking a fruitcake turns out to be quite useful. Both “materials” contain solid inclusions (aggregates in concrete, versus fruit or nuts in a fruitcake) and a binder (cement versus dough). In both cases, the consistency of the “batter” may be improved by adding water, and as a result, the porosity of the final product is increased. While in the case of fruitcake this porosity may be an advantage, particularly if the recipe calls for soaking the cake with brandy or kirsch after baking, it can prove catastrophic to the durability of concrete. Indeed, it is through the porous network of the cement paste that chemical agents can enter concrete and cause its degradation. Furthermore, increased porosity of the matrix significantly decreases concrete strength.

At first glance, this may suggest that the solution for a more durable concrete is

simply to add as little water as possible. However, while the amount of water required for complete hydration is ~25–30% of the cement mass, about twice this amount is needed to achieve sufficient workability. This is where dispersants, referred to in this field as superplasticizers or high-range water-reducing admixtures (HRWRAs) come into play. Indeed, the introduction of such admixtures in concrete has enhanced the durability, increased the strength, and improved the workability to levels that previously were unattainable.

## Benefits of Using HRWRAs in Concrete

In this section, the practical advantages to the construction sector of using high-range water-reducing admixtures are outlined. The mechanisms by which these advantages are achieved in materials terms are discussed in the following sections of this article.

## Self-Leveling / Self-Compacting Concrete

Nowadays, it is possible to optimize the properties of fresh concrete with the use of superplasticizers to combine a high flowability at very low additions of water with negligible segregation of the particles. This type of concrete, which is usually referred to either as self-compacting concrete (SCC) or self-leveling concrete (SLC), can be cast into a frame of reinforced steel without the need for the labor-intensive vibration usually associated with concrete placing. The introduction of SCC in the last few decades has enabled the development of new construction technologies. For example, the speed of construction of the 238-m-high Roppongi Hills Mori Tower in Tokyo is illustrated in Figure 1. In this case, the building structure consists of steel tubes, 2 m in diameter, which were filled with concrete to increase dimensional stability. The use of SCC made it possible to cast sections of up to 100 m in height without segregation of the aggregates due to gravity.

## Ecological Benefits

Superplasticizers are able to reduce the porosity of the final material by allowing the concrete to become workable with less water. This greatly enhances the durability of the concrete, which extends the life cycle of the infrastructure in which it is used, thereby reducing the ecological impact of the construction sector.<sup>1</sup> Furthermore, superplasticizers also make it possible to substitute substantial volumes of cement with industrial-waste materials such as slag, fly ash, and silica fume, which reduces the CO<sub>2</sub> emissions associated with cement production.

## Architectural Benefits

Concrete, while relatively inexpensive, is unique as a building material because it can be cast in a wide variety of shapes and sizes. Furthermore, because the use of superplasticizers improves workability and mechanical properties through water reduction (see the article by Vernet in this issue), architects can now exploit completely new designs for elegant structures with normal load-bearing capacities.

## Need for Predictability and Robustness

The benefits mentioned here produce a market drive for higher-performance concrete with enhanced workability. However, as performance requirements rise, the robustness of the mix design becomes a more critical issue. This brings with it a growing need for predictability in concrete properties and the *a priori* selection of concrete components as well as their proportioning,

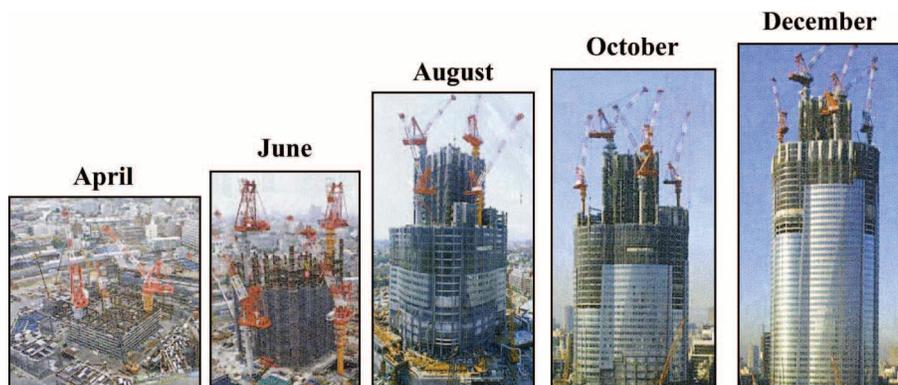


Figure 1. Series of photographs showing the speed of construction of the 238-m-high Roppongi Hills Mori Tower in Tokyo (completed in 2003). The use of self-compacting concrete made it possible to cast sections of up to 100 m in height without segregation of the aggregates due to gravity. (Photographs courtesy of M. Danzinger; personal communication).

in order to match the requirements of the design while minimizing sensitivity to variations in materials supply.

## Concrete Rheology and the Role of Superplasticizers

### Nature of Superplasticizers

The original introduction of superplasticizers into concrete was accidental. Carbon black had been added to concrete to change the color of the center line of a three-lane highway. In doing so, the concrete had poor workability, and a dispersant was introduced to counter the effect of the carbon black. The resulting hardened concrete showed properties that indicated that the cement had been positively affected by the dispersant;<sup>2</sup> the workers probably had added less water because of the enhanced dispersion, and thus higher strength was obtained in the hardened material. It is now common practice to use these additives to improve the flowability and extend the working time of fresh concrete.<sup>3,4</sup> The use of the first generation of superplasticizers—for example, sulfonated naphthalene formaldehyde (SNF) and modified lignosulfonates (LSs)—resulted in significant improvements in the properties of fresh concrete, and they are still widely used. However, increasing demands for better flowability, extended working time, and a reduction in concrete porosity have created a need for superplasticizers with improved performance.

### Dispersion Mechanisms

Superplasticizers adsorb at the solid-liquid interface between the particles and the aqueous phase. There, they impart a repulsive interparticle force, thus reducing or eliminating adhesion between particles in close proximity.<sup>4</sup> The attractive

forces between the cement grains, silica fume, fly ash, and slag particles may originate from van der Waals<sup>5</sup> or electrostatic forces (ion correlation, see the article by Pellenq and Van Damme in this issue), or from surface-charge inhomogeneities.

The term electrosteric stabilization is often used to describe how superplasticizers act as dispersants. Electrosteric stabilization is a combination of an electrostatic double-layer repulsion and a steric repulsion, where the relative importance of the respective contributions is closely related to the polymer segment density profile at the interface, the charge density of the polymer, and the ionic strength of the solution. To prevent particles from coming into close proximity with each other, this force must be sufficiently long-range. In cementitious systems, where the ionic strength is high ( $\sim 0.1$  mol/L), electrostatics alone do not suffice. Thus, it is expected that extending the layer thickness of adsorbed superplasticizers should improve their rheological performance in such systems.<sup>6,7</sup> This may be achieved with comb-type superplasticizers in which adsorption is driven by the ionic content of the backbone and the steric layer is enhanced by grafted non-adsorbing side chains that extend into the solution (Figure 2).

### AFM for Probing Properties of Adsorbed Polymers

From the previous discussion, it is clear that an important factor in the dispersion efficiency of superplasticizers is their adsorbed conformation. While computational methods such as molecular dynamics may provide insight into such phenomena in the long term, it is currently more practical to measure the interaction between superplasticizer-coated surfaces directly

in relevant solution conditions. The atomic force microscopy (AFM) method for measuring surface forces was first used by Ducker et al.<sup>8</sup> They attached a spherical particle at the tip of the cantilever and obtained a force-displacement curve from the deflection of the cantilever as a function of intersurface separation. This versatile method was recently extended to spherical MgO particles,<sup>9,10</sup> which have a similar surface chemistry as cement but have the advantage of being much less reactive when subjected to water.<sup>11</sup>

Figure 3 shows the results from direct-force measurements between a spherical MgO probe attached to the cantilever and a flat MgO substrate immersed in an aqueous media at pH 10.<sup>12</sup> It was found that the interaction is repulsive in a simple monovalent electrolyte (KCl), which probably can be related to the positive charge on the MgO surfaces (Figure 3a) and low attractive van der Waals forces. However, the addition of calcium resulted in an attraction between the surfaces that may originate from ion correlation forces, as described in the article by Pellenq and Van Damme in this issue. The addition of a comb-like copolymer having a negatively charged backbone with grafted poly(ethylene oxide) (PEO) chains of a relatively short length (PCP1) resulted in a stronger repulsion between the surfaces (Figure 3b). No attraction was observed, even in a calcium-rich electrolyte.

Addition of a comb-like copolymer having an identical backbone to PCP1 but with PEO side chains of a much longer length (PCP4) results in an interparticle repulsion that is much more long-range (Figure 3c). In addition, the effect of this polymer is influenced relatively little by the nature of the polyelectrolyte. This indicates that the steric repulsion is dominating and we can even get an indication of the thickness of the adsorbed layer on the surface. These results are currently being used in the design of superplasticizers with an optimal structure and can also be used for realistic estimates of the interparticle forces in larger-scale simulations of the rheology of particulate suspensions, as described in the section on "Interparticle Interactions/Yield Stress."

### The Role of Particle Size Distribution

While the addition of superplasticizers greatly improves concrete rheology through dispersion of the finer particles, the granular nature of concrete must not be overlooked.<sup>13</sup> Concrete contains particles of different types, spanning several orders of magnitude in size ( $\sim 50$  nm for silica fume to  $\sim 50$  mm for the largest aggregates). Thus, rheology

may be improved by better grading and proportioning of the components.<sup>14,15</sup>

**Incompatibilities**

While dispersion mechanisms appear well understood in general terms, many

details remain unresolved, in particular, cement–superplasticizer incompatibility.<sup>3</sup> This term refers to specific combinations of cement and superplasticizers that show poor rheological properties unless excessive amounts of polymer are added, or for

which the duration of the dispersion effect is extremely short.

These incompatibilities arise from the reactivity of cement and in particular from the calcium aluminate phases, which have the strongest initial reaction in the presence of water. The influence of the cement chemistry on superplasticizer performance is well established<sup>4,16</sup> and is attributed in part to the intercalation of the superplasticizers into hydration products.<sup>17</sup> The intercalated polymer is lost for dispersion purposes and this decreases efficiency.<sup>18</sup> In other cases, the efficiency of some polycarboxylates can be lowered because of competitive adsorption from sulfate ions.<sup>19</sup>

**Modeling**

A detailed simulation of concrete rheology, accounting for the motion of the cement, sand, and aggregates, is impossible on present-day computers. To solve the computational problem of the broad span of particle sizes in concrete, a multiscale or homogenization approach is used. Phenomena are modeled at a characteristic length scale to determine an average property, which is then used as an input in a simulation at a coarser scale. For example, if the viscosity of a mortar can be determined by simulation or experiment, that viscosity can be used as an input to determine the viscosity of concrete.

There are problems with this approach, mainly linked to agglomeration.<sup>20</sup> However, at sufficiently high shear rates, the evolution of an agglomerating system is similar to that of a non-agglomerating system. For cementitious materials that exhibit a Bingham behavior (a linear relation between shear stress and shear rate), plastic viscosity is the most relevant rheological parameter, and the slope of experimental flow curves can be compared to those of simulations.

**Suspensions Model Based on Dissipative Particle Dynamics**

While some analytical solutions describing the rheological properties of simple suspensions exist (e.g., for very dilute suspensions), understanding the flow of more complex suspensions like cement-based materials—dense suspensions and suspensions composed of particles with different shapes or particles that interact—remains a challenge. A major difficulty in modeling complex fluids like suspensions is the tracking of boundaries between the fluid and solid phases. Recently, a promising new computational method called dissipative particle dynamics (DPD)<sup>21</sup> has been developed for modeling complex fluid systems. Indeed, DPD may have advantages over other computational fluid

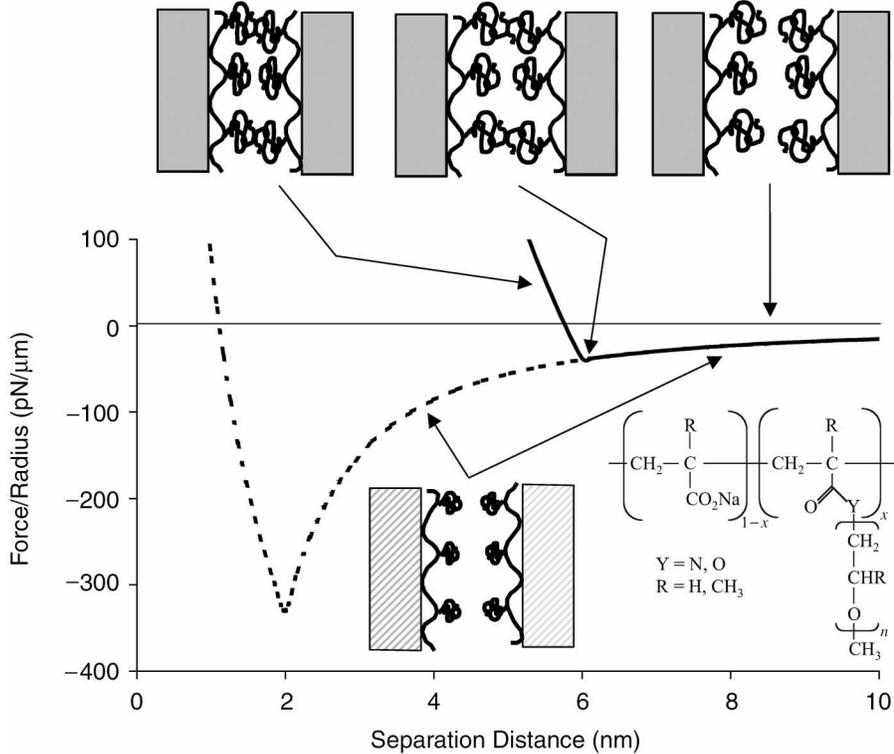


Figure 2. Schematic illustration of the force between two surfaces with adsorbed comb-like copolymers, as a function of separation distance. Steric repulsion prevents van der Waals interactions from developing strong attractive forces (negative values). Schematic illustrations (top) show surfaces (from right to left) before, at the onset, and during the overlap of their adsorbed layers, leading to steric hindrance that overcomes the van der Waals force. The dashed line in the graph is for a thinner adsorbed layer, which is shown before overlap-upon-layer-overlap in the lower illustration. The structure inset at lower right gives the generic composition of such comb-type copolymers.

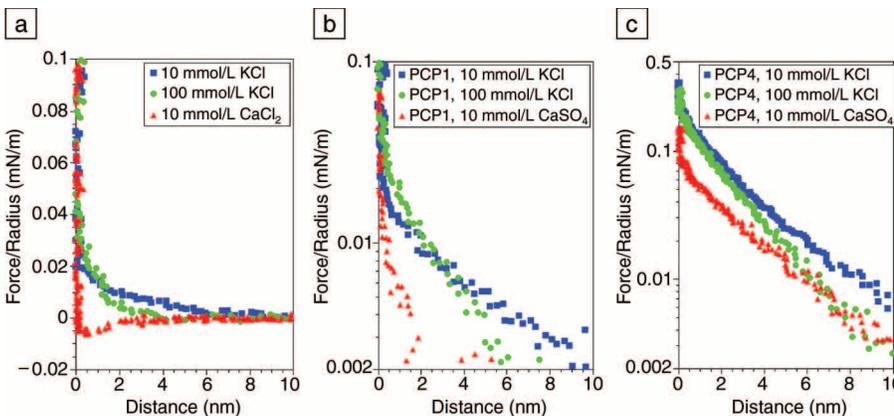


Figure 3. Atomic force microscopy colloidal probe results between MgO surfaces at pH 10: (a) without superplasticizer, (b) in the presence of PCP1 [short side chains of poly(ethylene oxide)], and (c) in the presence of PCP4 (longer side chains of PEO). The errors on such measurements are about 5 μN/m.<sup>13</sup>

dynamics methods because it can describe moving boundaries without requiring re-gridding of the computational domain.<sup>22</sup>

On the surface, DPD looks similar to a molecular dynamics algorithm,<sup>23</sup> where particles, subject to interatomic forces, move according to Newton's laws. However, the particles in DPD are not atomistic but instead are a mesoscopic representation of the suspension. The interactions between the particles are described by three classes of forces: conservative, dissipative, and random. The conservative force is a central force, derivable from some potential. The dissipative force is proportional to the difference in velocity between particles and acts to slow down their relative motion, producing a viscous effect. The random force (usually based on a Gaussian random noise) helps reproduce the temperature of the system while producing a viscous effect. Finally, it has been shown that DPD equations can account for hydrodynamic behavior consistent with the Navier–Stokes equations.<sup>24,25</sup>

To model a rigid-body inclusion in a fluid, a subset of the DPD particles are initially assigned a location in space such that they approximate the shape of the object.<sup>26</sup> The motion of these particles is then constrained so that their relative positions never change. The total force and torque are determined from the DPD particle interactions, and the rigid body moves according to the Euler equations.

Cement-based materials are usually composed of particles with a broad shape and size distribution. Figure 4 shows some typical examples. Figure 4a is a system of polydisperse spheres that could correspond to a concrete composed of riverbed aggregates, which are usually rounder and smoother than most aggregates. Figure 4b is based on realistic images of aggregates acquired by x-ray microtomography of a crushed aggregate. The tomographic images of aggregates can be analyzed for their geometrical properties by constructing a spherical harmonic representation of their shape.<sup>27</sup> Once the aggregate images are incorporated into the code, we can determine the viscosity of the total system relative to the matrix fluid viscosity for a given shear rate.

So far, we have found good agreement with experimental studies of the plastic viscosity of fresh concrete having an aggregate composition similar to that used in the simulations<sup>28</sup> (Figure 5).

## Interparticle Interactions/Yield Stress

We are currently investigating the incorporation of interparticle interactions that account for agglomeration of cement par-

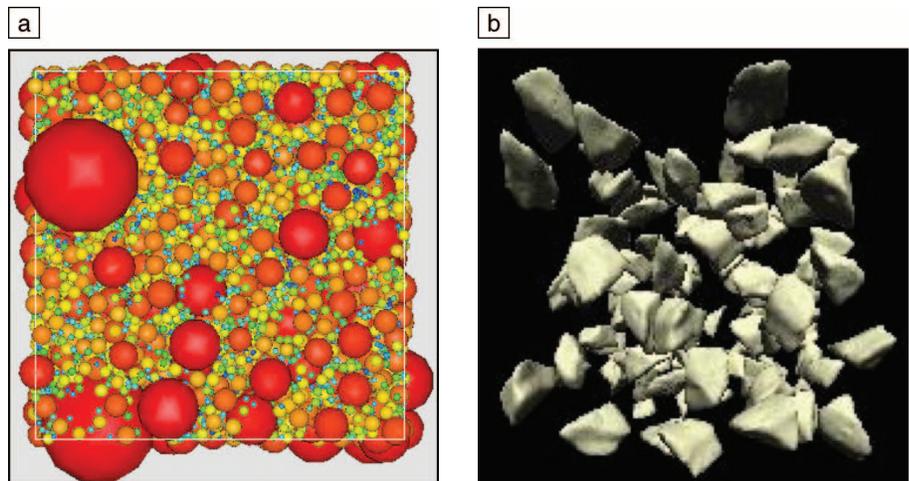


Figure 4. Example of concrete systems: (a) system of polydisperse spheres, corresponding to a concrete composed of riverbed aggregates, which are usually rounder and smoother than most aggregates; (b) model based on three-dimensional images of realistically shaped particles, acquired by x-ray microtomography of crushed aggregates.

ticles. For example, by including an approximation to the attractive van der Waals force expected in cementitious systems,<sup>5</sup> it is possible to produce a Bingham-like behavior in our suspension. To model the steric hindrance of dense layers, where interpenetration is low before the van der Waals force is counteracted, a cutoff distance is introduced at close separation. While more refined models need to be developed, the results of these preliminary

investigations are encouraging. Ultimately, we expect to be able to use conformational data of adsorbed superplasticizers from AFM within such predictions.

## Conclusions

In this article, we have highlighted two key aspects of concrete rheology: (1) the agglomeration of the finer particles and the role of dispersants to counter this agglomeration and (2) the granular nature of concrete and the role of particle size distributions on the rheological properties of concrete.

Mastering both aspects has led to significant progress in concrete technology, raising expectations for concrete properties and highlighting questions of robustness. Consequently, there is an increased need for predicting concrete properties and their variation.

In this context, modeling can play a crucial role. The work presented shows promising results in its ability to account for the three-dimensional shapes of particles. While good predictions of plastic viscosity have been obtained, more work is needed to accurately measure the role of yield stress. Ultimately, the model should use structural information about the superplasticizer molecule to properly evaluate interparticle forces. Such tools will not only allow better use of existing materials but will also help admixture producers design superplasticizers with better performance and enhanced robustness.

The utility and predictive capability of the models will improve with further advances in our ability to quantify interparticle forces and formulate multiscale models. In the long term, to properly describe cement

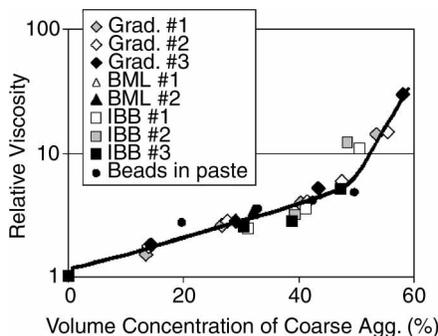


Figure 5. Comparison of relative plastic-viscosity values from a simulation of coarse aggregate gradings and experimental measurements using different concrete rheometers. In the figure, Grad. #1, #2, and #3 correspond to gradations of spherical aggregates used in the computer simulation. BML is a coaxial concrete rheometer, IBB is a vane concrete rheometer, and "beads in paste" corresponds to measurements of monosized glass beads in a cement paste using a parallel plate rheometer. The solid line is included as a guide for the eye.<sup>28</sup>

rheology, the inclusion of other features such as the reactivity of cement and the perturbation of dispersant efficiency through intercalation or adsorption competition from other species needs to be taken into account.

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